

**ADMINISTRATIVE INFORMATION**

1. **Project Name:** Development of Combinatorial Methods for Alloy Design and Optimization
2. **Lead Organization:** University of Tennessee  
404 Andy Holt Tower, Knoxville, TN 37996-0140  
Congressional District - 2<sup>nd</sup> Tennessee
3. **Principal Investigator:** George M. Pharr (pharr@utk.edu, phone 865-974-8202;  
fax 865-974-4115)
4. **Project Partners:** Oak Ridge National Laboratory, Dr. Easo P. George  
(georgeep@ornl.gov, phone 865-574-5085), Dr. Michael L.  
Santella (santellaml@ornl.gov, phone 865-574-5085)  
Duralloy Technologies, Dr. Roman Pankiw  
(techmgr@duralloy.com, phone 724-887-5100)
5. **Date Project Initiated:** April 1, 2002
6. **Expected Completion Date:** March 31, 2005

**PROJECT RATIONALE AND STRATEGY**

7. **Project Objective:** The objective of the program is to develop a comprehensive methodology for designing and optimizing metallic alloys by combinatorial principles. The basic concept is to develop a technique that can be used to fabricate an alloy specimen with a continuous distribution of binary and ternary alloy compositions across its surface - an "alloy library" - and then use spatially resolved rapid probing techniques to characterize the structure, composition, and relevant properties of the library.
8. **Technical Barrier(s) Being Addressed:** Traditional methods for alloy design and optimization are inherently time consuming, expensive, and unavoidably restrictive in the range of alloy composition that can be examined. Combinatorial methods promise to significantly reduce the time, energy, and expense needed for alloy design. The key technical barriers are to develop: (1) techniques for producing a large number of alloys quickly and inexpensively; and (2) techniques for rapidly characterizing the structure and properties of the alloys. If successful, the new techniques will be applicable to a wide variety of alloys, thus leading to improved materials for a large number of industries that rely heavily on metals. These industries include: aluminum, chemicals, forest products, glass, metal casting, petroleum, steel, forging, heat treating, and welding.
9. **Project Pathway:** Alloy libraries are being produced by three separate methods: (1) vapor deposition of discrete thin films of the component species on an inert substrate that are subsequently alloyed together by solid-state diffusion; (2) co-deposition of materials from three simultaneously operated RF magnetron sputtering sources; and (3) localized melting of thin metal films into underlying metal substrates by electron beams and lasers. The structure, composition, and properties of the specimens are being characterized by electron microprobe analysis, synchrotron x-ray diffraction, and nanoindentation. As proof of principle, the methodology is being applied to the Fe-Ni-Cr ternary alloy system that constitutes stainless steels and the commercially important H-series and C-series heat and corrosion resistant casting alloys.

10. **Critical Technical Metrics:** There are two critical technical metrics for the program. The first is to demonstrate that a technique capable of producing ternary alloy libraries spanning a wide range of composition can be successfully developed. This is now complete. The second is to develop techniques that can rapidly assess the structure and relevant properties of the libraries. Structural characterization techniques based on synchrotron x-ray diffraction have been developed. Ongoing activities and work in the next year will focus on rapid property measurement.

## **PROJECT PLANS AND PROGRESS**

### **11. Past Accomplishments:**

#### Year 1 (April 1, 2002 - March 31, 2003)

- *Designed and constructed controllable shutter system for the electron beam vapor deposition system in which alloy libraries are made.*
- *Determined optimum conditions for depositing wedge shaped films of iron, chromium, and nickel onto sapphire substrates to make a tri-layer specimen.*
- *Deposited iron, nickel and chromium films of uniform thickness (about 1 micrometer) on sapphire substrates to systematically identify conditions under which alloying can be achieved by solid-state diffusion.*
- *Examined quality of the first ternary alloy library using microfocus x-ray techniques at the Advanced Photon Source at Argonne National Laboratory.*
- *Began to explore alternative methods for alloying based on melting with an electron beam welding unit and a high-powered pulsed laser system.*

#### Year 2 (April 1, 2003 - March 31, 2004)

- *Developed a procedure to reduce the formation of oxides in ternary alloy libraries.* The procedure is based on annealing in an evacuated quartz tube back filled with a Ar/H<sub>2</sub> mixture and the specimen wrapped in tantalum foil to getter the trace oxygen.
- *Completed structural characterization of the ternary alloy libraries made by discrete layer deposition and interdiffusion using the newly developed synchrotron x-ray techniques.* New synchrotron studies revealed that the annealed libraries are of good quality, with the composition range spanning the entire ternary system and all of the expected phases appearing in approximately the right places.
- *Developed a new capability for making ternary alloy libraries based on co-sputtering from three separate magnetron sputtering sources operated simultaneously.* This preparation technique has the advantage that intermixing by diffusion and annealing is not needed after deposition, but is limited in the compositional spread that can be achieved. The technique was used to prepare five alloy libraries on 4 inch diameter sapphire wafers at substrate temperatures varying from 20°C to 800°C. The structure of the libraries characterized by synchrotron x-ray diffraction revealed that a distinct non-equilibrium phase forms in the alloys deposited at low temperatures but not at temperatures above approximately 400°C. The phase has the unusual  $\alpha$ -manganese structure. These studies have demonstrated that by varying the substrate temperature, one has the ability to create alloy libraries covering a wide range of equilibrium and non-equilibrium structures.
- *Conducted metallographic studies to explore the utility of pulsed laser melting as a tool for alloying thin films of chromium into nickel substrates.* These studies revealed that there is significant depletion of chromium due to vaporization and a strong tendency for the chromium films to crack and delaminate. We have concluded that laser melting is not an attractive method for alloying, at least in the chromium-nickel system.
- *Measured mechanical properties of alloy libraries by nanoindentation.* This effort has produced data sets that are large and unwieldy, so computer programs are under development to automate data reduction and graphical presentation. Initial results show that there are discernable differences in the hardness and elastic modulus within the library that correlate well with composition. For example,

it is clear that the region of the library associated with the sigma phase that appears in many of the unannealed films is very hard, as would be expected based on its complex crystal structure.

- *Melted thin films of chromium on nickel substrates by electron beam welding to examine the utility of this alloy library preparation technique and conducted a systematic study to identify the e-beam welding parameters needed to vary the composition of the melt pool over a range of composition.* This is also work in progress. Metallographic and EDX examination of the specimens is being used to establish the local chemical compositions and the degree of chemical homogeneity in the structure. Nanoindentation studies to measure the mechanical properties are also underway.
- *Prepared several bulk Fe-Ni-Cr alloys several by arc-melting and casting.* These will be used for comparison of the structure and properties of alloy libraries to conventionally alloyed materials.

#### 12. Future Plans:

- *Complete measurement of alloy library mechanical properties by nanoindentation* (completion by 6/30/04)
- *Assess carburization characteristics of alloy libraries* (completion by 12/31/04)
- *Assess corrosion resistance of alloy libraries* (completion by 12/31/04)
- *Measure relevant properties of bulk materials for comparison to alloy libraries* (completion by 12/31/04)
- *Prepare final report* (completion by 3/31/05)

#### 13. Project Changes:

Studies were undertaken in the past year to explore the utility of pulsed laser melting as an alloying tool for cutting thin metal films into a metal substrate. The materials system consisted of chromium thin films vapor deposited onto polished nickel substrates. In principle, the extent to which the chromium cuts into the substrate can be controlled by means of the laser power, pulse duration time, number of pulses, and laser spot size. However, it was found that the film preferentially vaporizes rather than melts, as might be suspected based on the relatively high vapor pressure of chromium. Furthermore, there is strong tendency for the chromium films to crack and delaminate. We have thus concluded that laser melting is not a viable method for alloying in the chromium-nickel system and have abandoned it in favor of e-beam melting.

Initial nanoindentation measurements of the mechanical properties of the ternary alloy libraries revealed that surface roughness can cause significant scatter in the data. However, it appears that a convenient way to deal with this problem is to measure the local contact stiffness. This parameter, which is directly related to the ratio of the elastic modulus to the hardness, is relatively insensitive to roughness, and can therefore be used as an important mechanical property metric when a relative rather than absolute measure is acceptable.

#### 14. Commercialization Potential, Plans, and Activities:

The product of this research will be a more efficient and less time consuming methodology for alloy design and optimization. Because conventional techniques for alloy preparation are unavoidably restrictive in the range of alloy composition that can be examined, combinatorial methods promise to significantly reduce the time, energy, and expense needed for alloy design. In addition to optimizing existing alloys, the combinatorial technique may result in the discovery of entirely new ones because large numbers of alloy compositions can be screened relatively quickly. Industry has been hindered in developing combinatorial alloy design methods largely because simple and effective techniques for fabricating and characterizing alloy libraries have not yet been developed. The sophisticated research equipment needed to accomplish these tasks is capital intensive and thus more likely to be found in universities and national laboratories than in industrial settings. In addition, most private companies do not have the in-house technical expertise needed to develop combinatorial methods.

While the research in progress is limited to one simple ternary alloy system, once the basic methodology is developed and validated in this project, it will be applicable to a wide variety of other alloys, thus leading to improved materials that crosscut the needs of a large number of industries. Among the industries that would be directly impacted are those relying heavily on metals and alloys, including, but not limited to: aluminum, chemicals, forest products, glass, metal casting, petroleum, steel, forging, heat treating, and welding.

Most of the work in this program is conducted by graduate students working on their dissertations. As such, the technology will be made readily available to a wide cross-section of potential end users through publication in the open literature. In addition, the direct interaction with the industrial partners provides a natural means for the technology to be transferred to an important end user. The ternary elements being investigated here form the basis of the important H-series alloys that are of interest to our industrial partners.

#### 15. Patents, Publications, Presentations:

##### Publications:

- (1) E.D. Specht, A. Rar, G.M. Pharr, E.P. George, P. Zschack, H. Hong, and J. Ilavsky, "Rapid Structural and Chemical Characterization of Ternary Phase Diagrams Using Synchrotron Radiation", *Journal of Materials Research* **18**, pp. 2522-2527 (2003).
- (2) A. Rar, E.D. Specht, E.P. George, M.L. Santella, and G.M. Pharr, "Preparation of Ternary Alloy Libraries for High-throughput Screening of Material Properties by Means of Thick Film Deposition and Interdiffusion: Benefits and Limitations", in press, *Journal of Vacuum Science and Technology*.
- (3) E.D. Specht, P.D. Rack, A. Rar, G.M. Pharr, E.P. George, and H. Hong, "Nonequilibrium Structures in Codeposited Cr-Fe-Ni Films", in press, *Materials Research Society Symposium Proceedings*.
- (4) A. Rar, E.D. Specht, H.M. Meyer III, M.L. Santella, E.P. George, and G.M. Pharr, "Preparation of Ternary Alloy Libraries by Means of Thick Film Deposition and Interdiffusion: Structure and Mechanical Properties", in press, *Materials Research Society Symposium Proceedings*.
- (5) A. Rar, E.P. George, M.L. Santella, E.D. Specht, J. Frafjord, P. Rack, J. Fowlkes, and G.M. Pharr, "Preparation of Ni-Fe-Cr alloy Libraries by PVD and High-throughput Property Characterization", submitted, *Journal of Measurement Science and Technology*.

##### Presentations:

- (1) "Preparation of Ternary Alloy Libraries for High-throughput Screening of Material Properties by Means of Thick Film deposition and Interdiffusion: Benefits and Limitations", Annual Meeting of the American Vacuum Society, Baltimore, MD, November 2003.
- (2) "Preparation of Ternary Alloy Libraries by Means of Thick Film Deposition and Interdiffusion: Structure of the Resulted Layer", Fall Meeting of the Materials Research Society, Boston, MA, December 2003.
- (3) "Nonequilibrium Structures in Codeposited Cr-Fe-Ni Films", Fall Meeting of the Materials Research Society, Boston, MA, December 2003.
- (4) "Development of Combinatorial Methods for Alloy Design and Optimization", ASM Materials Solution Conference & Show, Columbus, Ohio, October 2004.